



Determination of hyperfine fields and atomic ordering in NiMnFeGe exhibiting martensitic transformation

Dariusz Satuła,
Krzysztof Szymański,
Katarzyna Rećko,
Wojciech Olszewski,
Beata Kalska-Szostko

Abstract. The hyperfine fields and atomic ordering in $\text{Ni}_{1-x}\text{Fe}_x\text{MnGe}$ ($x = 0.1, 0.2, 0.3$) alloys were investigated using X-ray diffraction and Mössbauer spectroscopy at room temperature. The X-ray diffraction measurements show that the samples with $x = 0.2, 0.3$ crystallized in the hexagonal Ni_2In -type of structure, whereas in the sample with $x = 0.1$, the coexistence of two phases, Ni_2In - and orthorhombic TiNiSi -type of structures, were found. The Mössbauer spectra measured with $x = 0.2, 0.3$ show three doublets with different values of isomer shift (IS) and quadrupole splitting (QS) related to three different local surroundings of Fe atoms in the hexagonal Ni_2In -type structure. It was shown that Fe atoms in the hexagonal Ni_2In -type structure of as-cast $\text{Ni}_{1-x}\text{Fe}_x\text{MnGe}$ alloys are preferentially located in Ni sites and small amount of Fe is located in Mn and probably in Ge sites. The spectrum for $x = 0.1$ shows the doublets in the central part of spectrum and a broad sextet. The doublets originate from the Fe atoms in the paramagnetic state of hexagonal Ni_2In -type structure, whereas the sextet results from the Fe atoms in orthorhombic TiNiSi -type structure.

Key words: X-ray diffraction • Mössbauer spectroscopy • martensitic transition • atomic ordering

D. Satuła[✉], K. Szymański, K. Rećko
Faculty of Physics,
University of Białystok,
1L K. Ciołkowskiego Str., 15-245 Białystok, Poland,
Tel.: +48 85 738 8167, Fax: +48 85 745 7223,
E-mail: d.satula@uwb.edu.pl

W. Olszewski
Faculty of Physics,
University of Białystok,
1L K. Ciołkowskiego Str., 15-245 Białystok, Poland
and ALBA Synchrotron Light Source,
Crt. BP 1413, Km. 3.3, 08290 Cerdanyola del Vallès,
Barcelona, Spain

B. Kalska-Szostko
Institute of Chemistry,
University of Białystok,
1 Hurtowa Str., 15-399 Białystok, Poland

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Introduction

The magnetostructural coupling plays a crucial role in magnetoresponse effects in systems with martensitic transitions and because of shape memory, magnetocaloric and magnetoresistance effects [1–5] leads to practical applications. One class of the materials exhibiting martensitic transformations is based on ternary alloys ($\text{MM}'\text{X}$, M, M' – transition metal, X – Si, Ge, Sn) with hexagonal Ni_2In -type structure. The martensitic transformation occurs between high-temperature hexagonal Ni_2In -type austenite and low-temperature orthorhombic TiNiSi -type martensite structures.

The basic ternary alloy NiMnGe crystallizes in the hexagonal Ni_2In -type structure ($P6_3/mmc$, 194) with the martensitic transition at 470 K to the orthorhombic TiNiSi -type structure ($Pnma$, 62) [6, 7]. Upon cooling, the martensite phase shows additional transition from paramagnetic to antiferromagnetic state at the Neel temperature $T_N = 346$ K with magnetic moment of about $2.3 \mu_B$ localized only on the Mn atoms. In the martensite phase of NiMnGe , the antiferromagnetic spiral structure is formed [6, 7]. Moreover, it was shown that the spiral structure changes to canted ferromagnetic one under applied high-magnetic field and magnetization of the NiMnGe system saturate at about 10 T [6]. Substitution of Ni

atoms by Fe allows controlling both the martensitic structural transition temperature and magnetic state of material [2]. All these studies indicate instability of the antiferromagnetic spiral structure and allow enhancement of the magneto-responsive properties. The magnetic state and temperature of the structure transformation should strongly depend on the kind and concentrations of the doped elements and also on their atomic order. In literature, there are only a few examples of alloys in which atomic orderings were fully determined. It is often assumed that the doped atoms locate at the crystallographic position of a deficient element forming ideally ordered alloy. The assumption, however, is not a rule. For example, in the alloys with DO₃ structure, the experimental results showed that the atomic arrangement is not a subject to such simple rules [8–10].

The aim of this study is the observation of the hyperfine fields in Ni_{1-x}Fe_xMnGe ($x = 0.1, 0.2, 0.3$) on Fe atoms in austenite and martensite phases and determination of their preferential occupancies using ⁵⁷Fe Mössbauer spectroscopy.

Results and discussion

The series of Ni_{1-x}Fe_xMnGe ($x = 0.1, 0.2, 0.3$) samples prepared from appropriate masses of the pure elements were melted in an arc furnace under protective argon atmosphere. The samples were powdered in a ball mill and were used for X-ray and Mössbauer measurements. The X-ray diffraction was carried out on SuperNova diffractometer produced by Agilent Technologies equipped with a source of Mo microfocused $K\alpha = 0.713067$ nm radiation. The measurements were carried out in the range of diffraction angles $5^\circ < 2\theta < 50^\circ$ with the step 0.0343° . All experiments were performed on small amount of powder fixed by Paratone® N (Hampton Research) oil to a nylon loop. The diffraction patterns were analyzed by the Rietveld method.

The X-ray diffraction spectra are presented in Fig. 1. The diffraction patterns for $x = 0.2$ and 0.3 can be indexed using single phase of the high-temperature austenite, whereas for the sample with $x = 0.1$, the coexistence of both austenite and martensite was observed. The analysis shows that mass ratio of the austenite/martensite phases are equal to $(26 \pm 4)\% / (74 \pm 18)\%$. The obtained lattice parameters of austenite and martensite phases are presented in Table 1 and agree well with the data published in literature [2].

Table 1. The lattice parameters of hexagonal austenite (a_h, b_h) and orthorhombic martensite (a_o, b_o, c_o) phases

| Lattice parameters [Å] | $x = 0.1$ | $x = 0.2$ | $x = 0.3$ |
|------------------------|-----------|-----------|-----------|
| a_h | 4.098(8) | 4.088(16) | 4.086(11) |
| b_h | 5.412(10) | 5.375(15) | 5.350(13) |
| a_o | 6.034(17) | | |
| b_o | 3.781(11) | | |
| c_o | 7.097(21) | | |

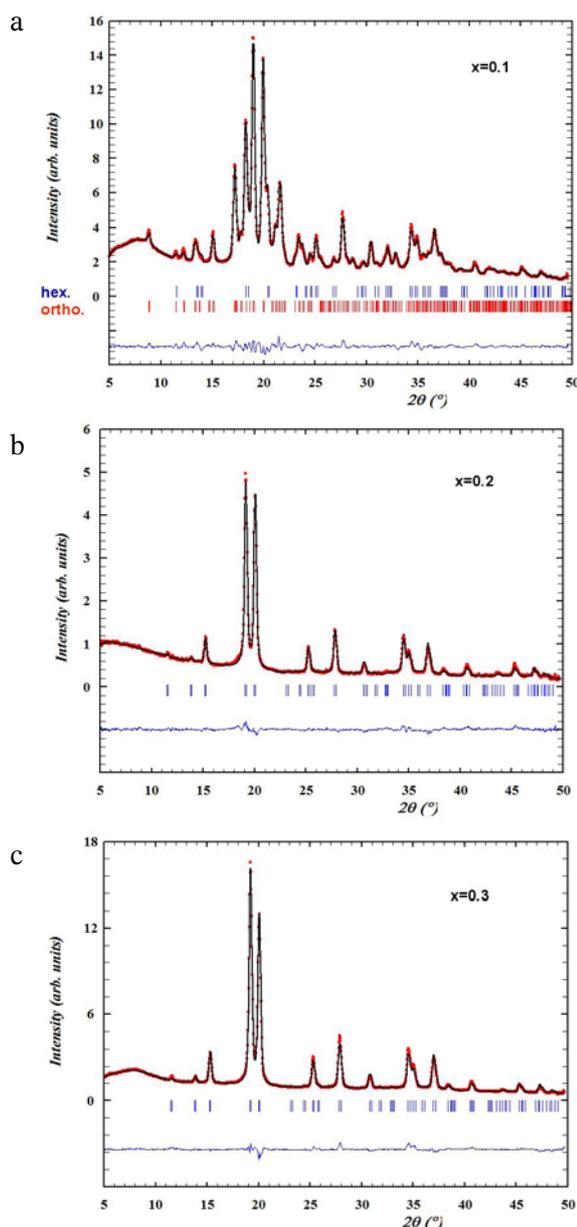


Fig. 1. The X-ray diffraction patterns for Ni_{1-x}Fe_xMnGe ($x = 0.1, 0.2, 0.3$). Solid line represents the best fit. Below the patterns, the Bragg positions and the residuals $I_{\text{obs}} - I_{\text{cal}}$ are shown.

The Mössbauer spectra were measured using standard spectrometer working at constant acceleration mode. The spectra measured at room temperature are presented in Fig. 2. The spectra were analyzed using the transmission integral procedure. The spectra for samples with $x = 0.2$ and 0.3 show superposition of the doublets for different local surroundings of Fe atoms while for $x = 0.1$, the additional broad sextet is present. Taking into account the results of X-ray diffraction, the doublets are due to different local surroundings of Fe atoms in the paramagnetic state of austenite and the broad sextet comes from non-resolved subspectra due to different local surroundings of Fe atoms at low-temperature martensite in the magnetic state. The hyperfine magnetic field found in ⁵⁷Fe atom probes have Gaussian distribution with mean value of $B = 8.9$ T and the standard deviation $\sigma_B = 1.3$ T. Using coupling

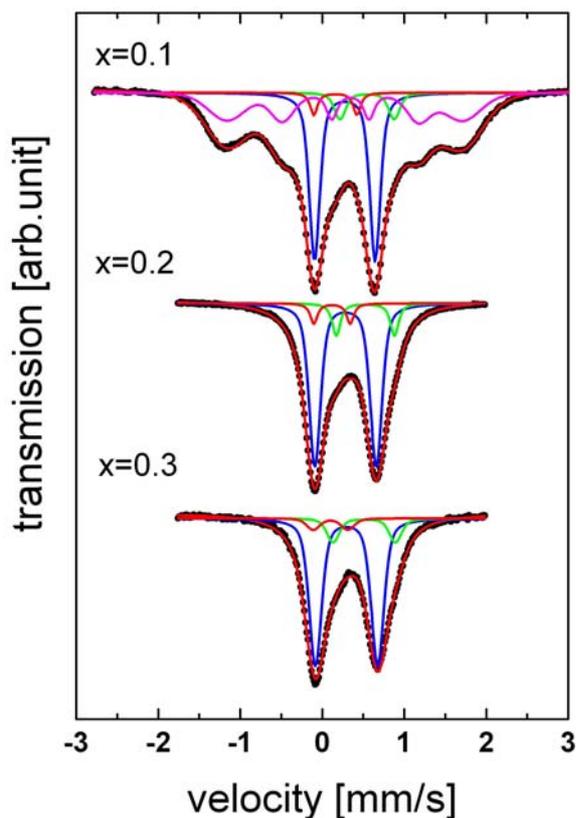


Fig. 2. Mössbauer spectra measured at room temperature. A solid line on the experimental points represents best fit. The spectra were analyzed using integral transmission procedure and the presented subspectra correspond to the cross-section of the individual components.

constant between hyperfine magnetic field and magnetic moments ($\sim 15 \text{ T}/\mu_B$ for $\alpha\text{-Fe}$) the estimated magnetic moment of Fe in TiNiSi phase is about $\sim 0.6 \mu_B$. In the hexagonal austenite NiMnGe alloy, Mn atoms are located at the $2a$ (0, 0, 0), Ni atoms at the $2d$ ($1/3, 2/3, 3/4$) and Ge atoms at the $2c$ ($1/3, 2/3, 1/4$) sites. In principle, three different positions can be occupied by substituted Fe atoms. The nearest local surroundings consist of (6Ni, 2Mn, 6Ge) (6Mn, 5Ge) and (5Ni, 6Mn) for Mn, Ni and Ge sublattice, respectively. The structure of the local surroundings within the distance of 3\AA from the origin for Mn, Ni and Ge sites in NiMnGe austenite are presented in

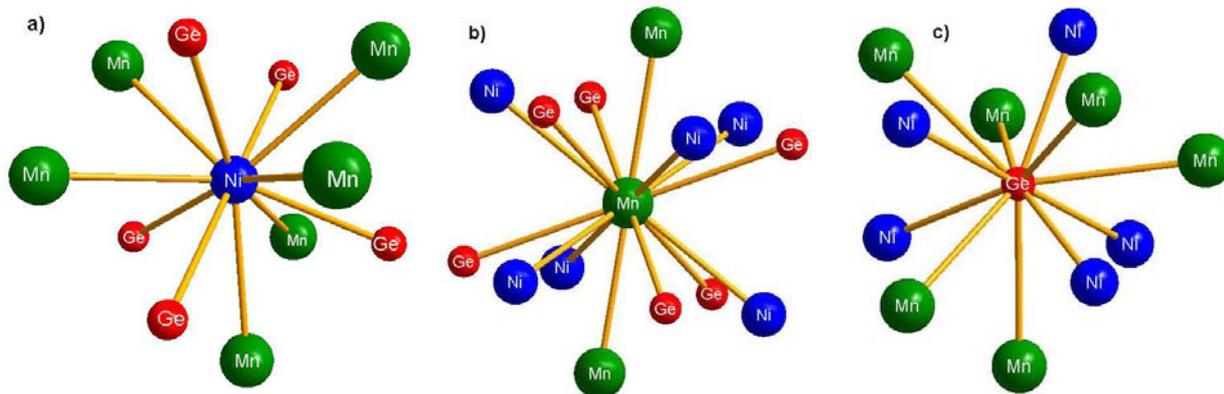


Fig. 3. The local atom configurations for NiMnGe alloy in the austenite phase for: a) Ni $2d$ site with (6Mn, 5Ge), b) Mn $2a$ site with (2Mn, 6Ni, 6Ge) and c) Ge $2c$ site with (6Mn, 5Ni).

Fig. 3. Because of low symmetry of the surroundings, one expects non-zero quadrupole interaction on the Fe atoms located in the austenite phase.

The spectra of samples with Ni_2In -type structure ($x = 0.2$ and 0.3) were fitted by three doublets for Fe atoms located in Ni, Mn and Ge sites, respectively. The results of isomer shifts, quadrupole splitting and relative intensities of the components are presented in Fig. 4. According to the study [11], the Ni and Ge atoms in the nearest neighborhood of iron in the Fe matrix increase isomer shift by about 0.02 mm/s and 0.06 mm/s , respectively, and Mn decreases it by 0.02 mm/s . These data allows one to estimate that Fe in the Mn position should have highest value of the isomer shift, equal to about 0.44 mm/s , Fe in Ni position about 0.18 mm/s , while Fe in Ge position lowest value of the isomer shift equal to about -0.02 mm/s .

The results of isomer shift and relative intensities of those three components allow identifying the Fe sites. The most-intensive doublet with the isomer shift of about 0.29 mm/s relates to the Fe in Ni positions (squares in Fig. 4). The component with highest value of isomer shift $\sim 0.5 \text{ mm/s}$ corresponds to Fe in Mn positions (circles in Fig. 4). The intensity of this doublet slightly increases with the increase of Fe concentration. The identification of these doublets was confirmed by Mössbauer measurements of the series of samples NiMnFeGe with deficiency of Mn for which the subspectra of Fe in Mn and Ni positions are much better resolved (not shown here, will be subject of a separate publication). The component with the smallest isomer shift $\sim 0.13 \text{ mm/s}$ is not well resolved and its intensity is small ($6 \pm 2\%$). This component may correspond to Fe in Ge position (triangles in Fig. 4). The small amount of Fe atoms in Ge positions can be due to very fast cooling of the sample after melting in the arc furnace. We do not exclude another interpretation, possibility of strongly correlated, narrow distributions of the quadrupole splitting and the isomer shift for Fe atoms in Mn and Ni position. Such assumption results in asymmetric doublets and a reasonably good description of the measured spectra. However, some extra free parameters have to be introduced. In order to clarify this point, the measurements on the annealed samples are planned. Irrespective of the interpretation of the origin of the

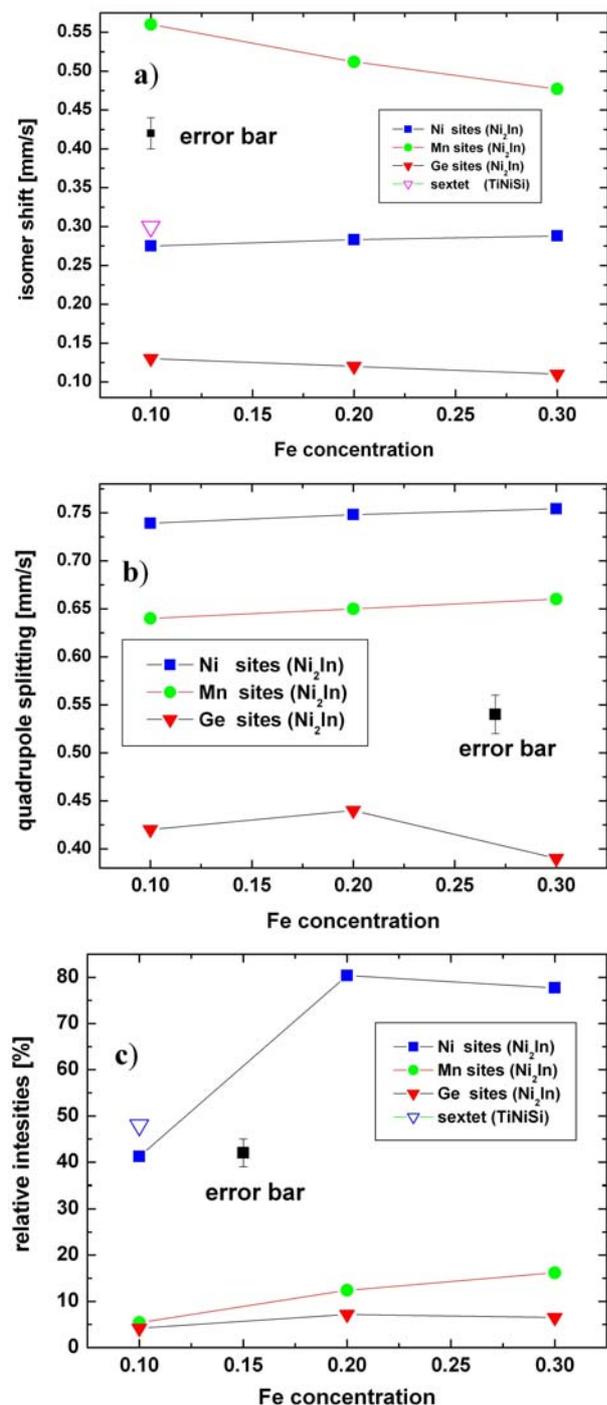


Fig. 4. a) The isomer shift, b) quadrupole splitting, and c) relative intensities of individual components obtained from analysis of the Mössbauer spectra.

additional component, obtained results lead to the conclusion that Fe atoms in the $\text{Ni}_{1-x}\text{Fe}_x\text{MnGe}$ alloys preferentially locate in the Ni sites.

The sextet for sample with $x = 0.1$, which corresponds to Fe in TiNiSi orthorhombic-type structure, shows broad distribution of the hyperfine magnetic field. Therefore, it was not possible to select individual components related to different local surroundings. In order to get better insight into physical phenomena the magnetization measurements are in progress.

Conclusion

In summary, the room temperature X-ray diffraction measurements show coexistence of the austenite and martensite phases in the sample with $x = 0.1$. The Fe atoms substituted to basic NiMnGe alloy decrease martensitic temperature of NiMnGe-based alloy from 470 K to the vicinity of room temperature. The samples with $x = 0.2$ and 0.3 crystallize in single austenite hexagonal phase at room temperature and are above the martensitic transition temperatures. The Mössbauer spectra for samples with $x = 0.2$ and 0.3 consist of three different doublets, which reflects three different positions of Fe atoms. The Fe atoms substitute preferentially for Ni atoms in $\text{Ni}_{1-x}\text{Fe}_x\text{MnGe}$ compound. Small amount of Fe locate in Mn and probably in Ge sites. The iron atoms in TiNiSi structure are in magnetic state with average hyperfine magnetic fields $B = 8.9$ T allowing for estimation of the iron magnetic moments at about $\sim 0.6 \mu_B$.

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